CO_2 deposition over the multi-year ice of the western Weddell Sea

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[1] Field measurements by eddy correlation (EC) indicate an average uptake of 0.6 g CO_2 m^{-2} d^{-1} by the ice-covered western Weddell Sea in December 2004. At the same time, snow that covers ice floes of the western Weddell Sea becomes undersaturated with CO_2 relative to the atmosphere during early summer. Gradients of CO_2 from the ice to the atmosphere do not support significant diffusive fluxes and are not strong enough to explain the observed CO_2 deposition. We hypothesize that the transport of air through the snow pack is controlled by turbulence and that undersaturation of CO_2 is caused by biological productivity at the ice-snow and snow-atmosphere interface. The total carbon uptake by the multi-year ice zone of the western Weddell Sea in December could have been as high as 6.6 Tg C y^{-1}. **Citation:** Zemmelink, H. J., B. Delille, J. L. Tison, E. J. Hintsa, L. Houghton, and J. W. H. Dacey (2006), CO_2 deposition over the multi-year ice of the western Weddell Sea, *Geophys. Res. Lett.*, *33*, L13606, doi:10.1029/2006GL026320.

[2] There is no doubt that the ocean plays a major role in regulating the concentration of atmospheric carbon dioxide (CO_2). *Takahashi et al.* [2002] and T. Takahashi (Ocean basin summations of sea-air flux computed using the 10 meter height winds, 2003, available at http://www.ldeo.columbia.edu/res/pi/CO2/carbondioxide/text/10m_wind.prn, hereinafter referred to as Takahashi, unpublished data, 2003) analyzed over 940,000 measurements of surface-water pCO_2 and estimated the annual net uptake of CO_2 by the global oceans to be 1.64 Pg C yr^{-1}. The Southern Ocean forms a significant sink for atmospheric CO_2; *Takahashi et al.* [2002] and Takahashi (unpublished data, 2003) estimated an uptake of 0.35 Pg C yr^{-1} south of 50°S for 1995, which is 21% of the global uptake. However, ice-covered oceanic zones are not taken into account in the current climatology. The role of ice-covered zones was ignored because it was assumed that sea ice precludes gas exchange [*Tréguer and Pondaven*, 2002]. However, recently, *Semiletov et al.* [2004] showed that invasion of atmospheric CO_2 could be significant over Arctic sea ice. In addition sea ice formation could enhance the uptake of atmospheric CO_2 [*Anderson et al.*, 2004]. In this study we present data on CO_2 fluxes over the multi-year ice zone of the western Weddell Sea.

[3] The study was performed during the 2004 Ice Station Polarstern (ISPOL) cruise, a field experiment designed to improve understanding of physical and biological air-sea-ice interactions in the Weddell Sea through early summer (November–December). ISPOL involved a 37 day drift station on an ice floe (from 68°15′S, 54°45′W to 67°22′S, 55°25′W) in the western Weddell Sea, the largest perennial ice-covered zone in the Southern Ocean.

[4] The CO_2 flux was measured at a height of 2.75 m using the eddy correlation (EC) technique. EC is considered to be the most direct technique for measuring gas fluxes [*Fairall et al.*, 2000], since it utilizes the covariance of scalar concentrations (or mixing ratios) and vertical wind velocity. EC requires measurements at a sufficient rate (10–20 Hz) to adequately capture all turbulence frequencies contributing to the flux. The EC system (Applied Technologies, Inc.) used in this study was battery powered and included a SATI/3K three-axis sonic anemometer and an open-path infrared CO_2/H_2O analyzer (Li-7500, Li-COR, USA). The battery pack and computers of the EC system were placed in a shelter at 20 m distance from the meteorological tower. Data acquisition and processing was to a large extent similar to those of EC measurements conducted in previous experiments as part of slow response techniques to measure DMS fluxes from the oceans [*Zemmelink et al.*, 2004a, 2004b; *Hintsa et al.*, 2004]. During ISPOL, post-processing of the data included coordinate rotation followed by application of the *Webb et al.* [1980] corrections to determine the latent and sensible heat fluxes from the measured mean covariances of vertical wind speed with sonic temperature and with water vapor density. These were then used to compute a density-corrected CO_2 flux with an averaging period of 30 min. Fluxes are indicated according to the micrometeorological convention, i.e., negative when directed downward.

[5] Instrumental failures during snowfall occurred and data during those episodes were discarded from further analysis. The source area of the flux was selected to exclude influence of the ship and the shelter; that is, measurements were only accepted when the ship and shelter were located downwind from the EC tower. The ice floe in the presumed fetch area was relatively flat (with the exception of some pressure ridges), with an adequate fetch of at least 300 m before the presence of a 10 m wide lead (open water). The 50% source area (determined following *Schmid* [1994]) for EC measurements at 2.75 m was well within the boundaries of the floe.

[6] The accuracy of the EC system can be derived by comparison of different techniques and sensors that were

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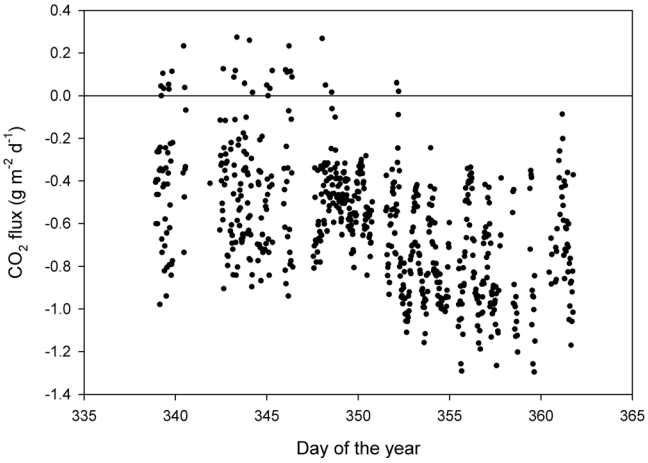

Figure 1. Turbulent CO_2 fluxes (g CO_2 m^{-2} d^{-1}) over the multi-year ice in the western Weddell Sea as measured by eddy correlation in December 2004.

used during ISPOL to measure latent heat (LH) and sensible heat (SH) fluxes respectively. LH fluxes derived from a bulk aerodynamic approach (using the temperature difference between snow and atmosphere) averaged 10 W m^{-2} (J. Launiainen, ISPOL meeting Tvärminnen, personal communication, 2006), while our EC measurements resulted in an average LH flux of 14.8 W m^{-2}, a difference of 50%. SH fluxes measured by EC by J. Launiainen averaged 5.9 W m^{-2}; our measurements averaged 4.7 W m^{-2}, a difference of 20%. Although this comparison shows reasonable agreement between independent measurements, it remains difficult to make statements about absolute accuracies. An underlying problem is that the techniques have different source areas with different surface characteristics that influence the flux. We estimate that the uncertainty of the covariance measurements presented in this study is 10–30%, which is comparable to the error estimates of previous experiments conducted at sea [*Edson et al.*, 1998; *Hintsa et al.*, 2004] and slightly higher than the uncertainty of land-based covariance flux measurements, which is typically on the order of 10–15%.

[7] The sonic anemometer was serviced and calibrated by the manufacturer prior to the beginning of the experiment. Zero calibration of wind speed and span calibration of temperature to −30°C showed that the anemometer was stable in the field. The Li-COR CO_2/H_2O analyzers were serviced and calibrated by the manufacturer at the beginning of the experiment. In the field, zero calibration (by chemical removal of CO_2 and H_2O) was performed every week and showed no drift. Experience has shown that a change in span is unlikely when zero calibration does not drift. Span calibration in the shore laboratory at the end of the experiment showed that drift of the instruments over the interval of the experiment was negligible.

[8] CO_2 concentrations in the snow were determined daily near the base of a meteorological tower. Two liters of air from a series of inlets at different depths in the snow were sampled through thick-walled Teflon tubing into Vac-U-Chamber airtight boxes (SKC Inc.), into which Tedlar bags were placed for sample accumulation. Several Vac-U-Chamber boxes could be evacuated with a single pump, and a three-way valve on each box allowed switching from purging the tubing to collecting air samples at 100 ml min^{-1} (for more details see *Hintsa et al.* [2004]). Subsequently, bags were brought back to the ship's laboratory and analyzed for CO_2 using a closed path Li-7000 in absolute mode. Toward the end of December, however, melting and refreezing changed snow conditions and it was decided to use a Li-6262 set up for direct measurements of CO_2 in the field by pumping air through the analyzer at 300 ml min^{-1}.

[9] Aerial photography and electromagnetic soundings around the selected floe (over a triangle of about 70 km along each side) revealed that the ice floe actually consisted of a mosaic of individual multi-year (probably second-year) ice floes welded together by areas of first-year ice, with frequent occurrences of deformation ridges at the boundaries. Snow thickness near the meteorological tower varied between 0.5 and 1 m, generally higher in the vicinity of ridges. A number of significant changes in the character of the pack ice between 29 November 2004 and 1 January 2005 were observed as described by *Zemmelink et al.* [2005].

[10] Briefly, during the first three weeks of fieldwork two types of snow were distinguished: snow that covered slush and snow that covered solid ice. Sudden changes in sea ice characteristics occurred toward the end of December, when melting of snow and surface flooding was observed and slush and melt ponds formed at the surface of the snow, in addition to an increase of slush between the snow and underlying ice. Refreezing of water in the snow resulted in the formation of granulated snow (containing small pieces of ice and open spaces) and of superimposed ice (refrozen snow melt as a layer of solid ice at some depth within the snow pack). Snow characteristics became very heterogeneous toward the end of December when the slush turned brown due to the abundance of diatoms.

[11] The discoloration of slush and melt ponds implies increasing primary production in and at the surface of the snow pack, which would lead to an uptake of CO_2 by the floe. Indeed, the daily flux, as measured by EC, increased from −0.2 g CO_2 m^{-2} d^{-1} in early December, to −0.8 g CO_2 m^{-2} d^{-1} toward the end of December, averaging −0.6 g CO_2 m^{-2} d^{-1} (Figure 1). Fluxes exhibited some variation, probably caused by surface heterogeneity, but also showed a diurnal cycle correlating with the heat flux (data not shown), with maxima around 15:00, especially apparent after year day 350. The observed carbon flux values are lower than fluxes measured by EC over fast ice of the North American-Siberian Arctic Ocean shelf zone [*Semiletov et al.*, 2004], ranging between −0.9−−1.7 g CO_2 m^{-2} d^{-1}. However, those fluxes were measured over sea-ice melt ponds and open brine channels known to be highly productive [*Thomas and Dieckmann*, 2002].

[12] From a numerical model *Arrigo et al.* [1997] concluded that primary production in ice of the Weddell Sea could average 1.4 g C m^{-2} $month^{-1}$ in December, increasing to 1.9 g C m^{-2} $month^{-1}$ in January. This is in agreement with our flux measurements ranging from 1.7 g C $m^{-2}month^{-1}$ (in early December) to 6.8 g C $m^{-2}month^{-1}$ (toward the end of December) with an average of 5.1 g C $m^{-2}month^{-1}$. Maximum growth of "sea ice algae" is reached in first-year ice and is near its peak in December when surface flooding provides nutrients at the ice-snow

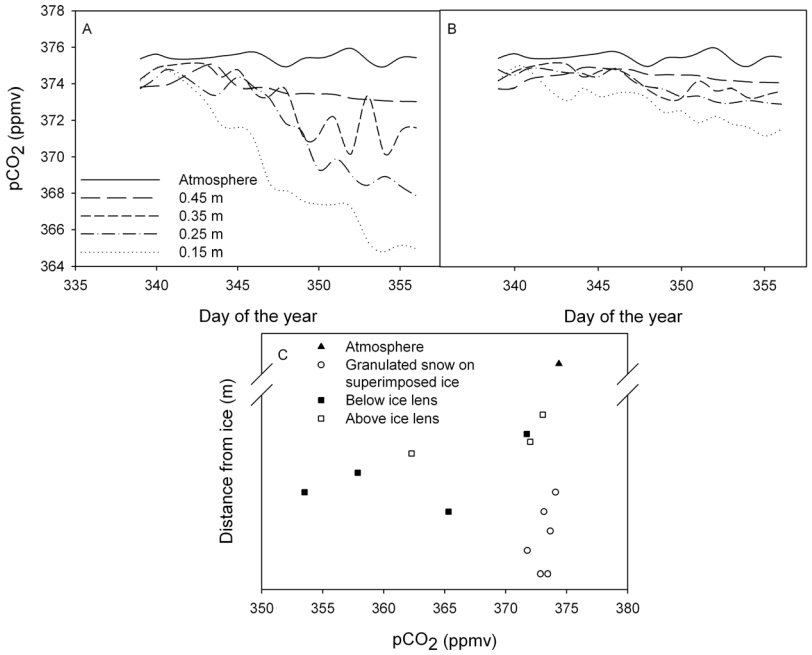

Figure 2. CO_2 concentrations (ppmv) in snow, as a function of distance from the ice surface, and in the atmosphere at 0.85 m from the ice. (a) Profiles over slush. (b) Profiles over solid ice. (c) CO_2 concentrations (ppmv) at three locations during the last week of December. Melting and freezing resulted in extremely heterogeneous snow characteristics, showing ice formation and inclination of snow layers.

interface and within the freeboard layer, near sea level [*Arrigo et al.*, 1997].

[13] Primary production could be hampered by slow replenishment of CO_2 through the snowpack, which tempers atmospheric turbulence. *Albert and Shultz* [2002] studied in situ transport of SF_6 in undisturbed snow in light (3 m s^{-1}) and moderately strong (9 m s^{-1}) wind conditions. Results indicated that transport in a hoar layer was diffusion-controlled at low wind speed, and more turbulence-controlled at the higher wind speed.

[14] Following *Takagi et al.* [2005], the diffusion flux (F_d) of CO_2 through the snow layer can be evaluated by Fick's law of diffusion $F_d = D_c\theta\lambda\Delta C/\Delta z$. The binary diffusion constant for CO_2 in air (D; $0.138*10^{-4}$ m^2 s^{-1} at standard temperature (T_0) and pressure (P_0)) was corrected for observed temperature (T) and pressure (P) to determine the diffusion coefficient (D_c) as, $D_c = D\ (P_0/P)(T/T_0)^{1.81}$. A fixed value of the air-filled porosity (θ) of 0.60 cm^3 cm^{-3} (averaged over ISPOL (C. Haas, personal communication, 2006)) was used to calculate the tortuosity factor λ ($\lambda = (1 - (1 - \theta)^{2/3})/\theta$). Using a concentration gradient ($\Delta C/\Delta z$) of CO_2 between the ice and atmosphere of 5.24 * 10^{-10} g_{CO2} $cm^{-3}{}_{snow}$ cm^{-1} (maximum gradient in the snow layer observed during ISPOL), the diffusive flux during ISPOL is about 37.8 mg CO_2 m^{-2} d^{-1}, which is in the same range of values found for diffusive transport through a snowpack as measured in a forest [*Takagi et al.*, 2005]. However, it is difficult to interpret our measured gradients and the derived diffusion controlled flux because sampling 2 L of air implies that the sample is pulled from a sphere with a radius of a least 8 cm. It is likely that the air is transported over some distance, depending on the resistance in the snow.

[15] The diffusive flux as found in *Takagi et al.*'s [2005] study and in this study is significantly lower than the flux measured by EC. Takagi et al. found that CO_2 concentrations in a snow pack fluctuated significantly as wind speeds increased from near zero to 2 m s^{-1}, which shows that wind-pumping strongly affects transport of CO_2 in a snowpack. Wind speeds during ISPOL varied between 1 and 14 m s^{-1}, averaging 5.3 m s^{-1}. It is therefore possible that the observed concentration gradients in the snowpack remained relatively small as a result of airflow within the snowpack, which makes turbulence the dominant transport factor and lowers the estimated influx by Fick's law. However, our study, during which measurements of CO_2 profiles in the snowpack were not made continuously, does not allow a detailed analysis of the dependence between CO_2 concentrations and wind speed as performed in the study of *Takagi et al.* [2005].

[16] Depletion of CO_2 in snow-encapsulated air is especially apparent above the brown colored slush (Figures 2a and 2b). Increasing productivity at this interface results in a further decrease of pCO_2 throughout the snow layer over the course of December. In addition, refreezing of meltwater and the formation of ice lenses toward the end of December will hamper turbulence in the snowpack and transport of CO_2. Figure 2c shows the strong undersaturation of CO_2 below an ice lens that impedes exchange with the atmosphere, while CO_2 utilization still occurs. Above another ice lens, uptake of CO_2 also occurs, but it is partially compensated by transfer from the atmosphere. No gradients of CO_2 where observed in coarse-grained granular snow, where turbulent transport of air may not be restricted by the open structure.

[17] We hypothesize that the measured fluxes during ISPOL are due to biological activity in slush, formed at the ice-snow interface, and biological activity at the snow-atmosphere interface, where flooding provides nutrients [*Thomas and Papadimitriou*, 2003]. Unfortunately, other

than observations of increasing brown discoloration at the snow surface and in brash ice and a diurnal cycle in the CO_2 flux, no data on primary production were collected to support this hypothesis.

[18] Assuming that the multi-year ice zone in the western Weddell Sea extends to 1.3 * 10^6 km^2 [*Gloersen et al.*, 1992] and an average carbon dioxide flux of -0.6 g CO_2 m^{-2} d^{-1} throughout December; the total carbon uptake in December alone in the multi-year ice zone could be as high as 6.6 Tg C y^{-1}. However, one cannot assume that this is going to remain below the ice: part of this carbon might well return to the inorganic carbon pool and atmosphere later in the year. *Hoppema et al.* [1999] calculated, from estimations of entrainment (introducing 34 Tg C y^{-1} into the 100 m surface layer) and new production (removing 42 Tg C y^{-1}), that the total uptake of atmospheric carbon by the Weddell Sea amounted to 8 Tg C y^{-1}. However, *Hoppema et al.* [1999] discuss that by extrapolating their results from the offshore area to the entire Weddell Sea they probably underestimate the effect of the biological pump. In addition, the budgets presented by *Hoppema et al.* [1999] are annual estimates; most of the atmospheric exchange will occur in the biologically productive months: December through February. Our calculated carbon uptake is in agreement with the values derived by *Hoppema et al.* [1999].

[19] The observed fluxes are significant beyond the local scale, as they amount to $\sim$1.8% of the total uptake south of 50°S as estimated by *Takahashi et al.* [2002] and Takahashi (unpublished data, 2003). Although this is a very crude estimate based on the assumption that the observed ice characteristics are representative of the entire perennial ice zone of the western Weddell Sea (and that biological activity in the flooded snow pack is a common feature), it suggests that this region plays an important role in the Southern Ocean CO_2 budget.

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